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AUTHORITY

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GENERAL

The Proceedings of the Air Force Materials Laboratory Fiftieth Anniversary Conference on Corrosion of Military and Aerospace Equipment, held in Denver May 23-25, 1967, have been issued.[1] Some seventy papers covering all aspects of corrosion are represented in their summary. The individual papers were reviewed in the two previous DMIC Reviews on Corrosion and Compatibility dated October 11, 1967, and December 15, 1967.

A literature survey on raindrop erosion has been released by Redstone Arsenal.[2] The survey concludes that rain erosion is expected to be very serious with most nose-cone materials when the missile nose-cone radius is less than 0.5 feet and it is passing through rain at velocities greater than 3000 ft/sec. Equations are available for estimating the penetration of individual raindrops into ductile metals and ablating surfaces at velocities to 30,000 ft/sec. Rain-erosion damage apparently is reduced as the thickness of the molten ablative material on the nose cone is increased. Nose-cone spikes have been effective in reducing rain-erosion damage at velocities of a few thousand feet per second.

The effect on corrosion resistance of boron-fiber strengthening of aluminum, copper, and nickel has been reported by Avco.[3] The boron either had no effect on, or slightly enhanced, the corrosion rates of these materials in chloride solutions or in air oxidation. In addition, the aluminum-boron composites showed a somewhat greater corrosion rate in buffered solutions at pH 8 and a slightly decreased rate at pH 4 and 10 (as compared with those without boron). The presence of boron in nickel accelerated the corrosion in aluminum sulfate solutions.

The effect of inhibitors on the corrosion of aluminum, magnesium, stainless steel, and titanium in N_2O_4 containing added water has been studied at the Aerospace Corporation.[4] Corrosion tests were conducted at 15.5 C (59.9 F) for periods ranging from 15 to 60 days. Ammonium fluorosulfonate (NH_4SO_3F) appeared to be the best of the inhibitors investigated. Other promising inhibitors were phosphorus pentafluoride, phosphorus trifluoride, and potassium fluorosulfonate. The long-term effects of the inhibitors on corrosion performance and their effects on propellant performance were not studied.

Impact data for aluminum and titanium alloys are being determined by McDonnell Douglas as part of a study on the engineering behavior of tankage materials in liquid propellants.[5] Standard ASMA open-cup impact tests (at 72 ft-lb) indicated that 2014-T6 aluminum was not impact sensitive in N_2O_4 or liquid fluorine but was impact sensitive in ClF_5 at temperatures between -50 C (-58 F) and the boiling point. -14 C (6.8 F). Modified ASMA open-cup impact tests revealed that Ti-6Al-4V alloy was not impact sensitive in N_2O_4, but was impact sensitive at 42.5 ft-lb in ClF_5 at -14 C.

CORROSION OF ALUMINUM ALLOYS

General

The effect of a deionized water rinse after sulfuric acid-sodium dichromate treatment on the adhesive-bonding characteristics of 2024 aluminum has been studied by Picatinny Arsenal.[6] Immersions greater than 15 minutes in deionized water at 60 C (140 F) produced an iridescent film on the aluminum and a subsequent loss in adhesive bondability. A hydrated oxide layer ($Al_2O_3 \cdot 3H_2O$) 1000 A thick was found on the surface of these specimens. Multivalent compounds added to the water were found to preferentially absorb into the aluminum oxide and block the entrance of water, thereby preventing hydration of the oxide. The addition to the deionized water (at pH below 5) of multivalent compounds such as H_2SO_4, $MgSO_4$, $CrCl_3$, $Na_2Cr_2O_7$, Na_2SO_4, $FeCl_2$, and $FeCl_3$ was recommended to give good bonding surfaces. Alkaline compounds such as $NaHCO_3$, Na_2CO_3, and K_2CO_3 were not recommended because they attack and discolor the aluminum.

Stress-Corrosion Cracking

Research on an accelerated stress-corrosion test for aluminum alloys is continuing at Kaiser.[7] A continuous immersion in 1 percent NaCl-2 percent $K_2Cr_2O_7$ solution at pH 4 and 60 C was found to be effective in separating the tempers of 2024, 2219, and 7075 alloys that exhibit borderline and maximum resistance to cracking in the short-transverse direction of fabrication. The salt-dichromate test made these separations in 1 week or less compared with 30 days in alternate immersion in 3.5 percent NaCl solution. C-ring specimens gave the best correlation between the two test methods. Tensile specimens (1/8-inch diameter) did not always give an aggressive test in the salt-dichromate tests specifically with the tempers of the 2219 and 7075 alloys which exhibited borderline resistance to cracking.

Research on the exfoliation and stress-corrosion characteristics of high-strength heat-treatable aluminum alloy plate has been summarized by Alcoa.[8] Specimens were evaluated in marine and industrial atmospheric tests and in acidified

dissolved titanium increased the corrosion resistance of ferrosilicon-extracted magnesium by a factor of 5 to 10. Saturation of electrolytic magnesium with titanium increased its corrosion resistance by a factor of 15 to 20, presumably because of the removal of iron.

CORROSION OF NICKEL-BASE ALLOYS

Half-cell potentials have been measured by the Marine Engineering Laboratory for nickel-base superalloys, several pure metals, nickel-chromium binary alloys, and several intermetallic compounds in molten NaCl and Na_2SO_4 at 1650 F.[17] Platinum was used as the reference electrode. Potentials for pure chromium and alloys containing more than 15 wt% chromium exhibited a marked positive change with time in the Na_2SO_4, but only a slight positive change in NaCl. The behavior in Na_2SO_4 was correlated with the formation of protective Cr_2O_3 oxide on the specimens, while that in NaCl was related to the rapid attack on chromium-containing alloys in this medium.

A summary report on the hot corrosion of nickel-base alloys has been issued by Allison Division of General Motors.[18] Each test consisted of 500 cycles at 1700, 1800, 1900, or 2000 F. A cycle consisted of a 0.5-minute spray of 1 percent sodium sulfate solution between 1.5-minute heating periods. A regression equation was derived which related metal loss to alloy chemistry. Chromium and aluminum were beneficial to corrosion resistance whereas tungsten and molybdenum were detrimental. The order of decreasing corrosion resistance of alloys studied was FDRL 163, IN-728NX, Alloy 713C + 2Cr + Y, Alloy 713 + 2Cr, Inco 717, Alloy 713C, Mar-M421 (14.6Cr), IN-100, GMR-235, and Mar-M235.

One years' results of a study of the hot corrosion of nickel-base and cobalt-base superalloys have been summarized by General Electric.[19] Alloys were exposed 500 to 1000 hours at 1600 to 2050 F to the exhaust gases from diesel fuel (1%S) which were injected with 5 ppm sea salt. Sulfidation was severe at 1600 to 1750 F, but was not a problem at temperatures above 1750 to 1800 F, presumably because Na_2SO_4 vaporizes at these temperatures. At 1600 to 1750 F, the commercial cobalt-base alloys were more corrosion resistant than the commercial nickel-base alloys. The best alloys were X-40 and Hastelloy X. The most corrosion-resistant cobalt-base alloys at 1900 to 2050 F were MELCO-2-9 and -10.

At General Electric, a mechanism study of the hot corrosion of superalloys in hot gases containing NaCl and SO_2 led to the conclusion that hot corrosion was the result of increased oxidation caused by the removal of chromium from the alloy matrix by the formation of chromium-rich sulfides.[20] As these sulfides become oxidized, the sulfur penetrated more deeply into the alloy, creating susceptibility to faster oxidation in their wake. Aluminum, cerium, and titanium additions to nickel-base alloys reduced corrosion in some instances, whereas cerium, lanthanum, and yttrium were beneficial in cobalt-base alloys.

CORROSION OF TITANIUM

General

The English have studied the ignition and burning of titanium alloys in connection with fires in the titanium compressor stages of gas turbine engines.[21] Some 39 binary alloys were ignited in oxygen. The ignition temperature of pure titanium was found to be 1417 C (2583 F). Significant changes in ignition temperature due to alloying are summarized below.

Alloy Composition, wt%	Difference from Ignition Value for C. P. Titanium, C
1.0 carbon	+65
6 copper	+63
5 iron	+70
34 molybdenum	+85
6 nickel	+63
0.1 sulfur	+98
0.5 silicon	+78
2 silicon	+80
46 tantalum	+88
30 tungsten	+98
10 silver	-54
13 copper	-64
22 manganese	-117
0.25 sulfur	-57
12 tin	-115
22 tin	-107
31 zirconium	-287

Although aluminum in titanium had no significant effect, the injection of aluminum powder into the stream lowered the ignition temperature by more than 100 C, thus tending to confirm that fires in titanium compressor blades are caused by rubbing against debris from aluminum blades in earlier stages of the compressor.

Stress-Corrosion Cracking

The proceedings of the 1-day seminar at Battelle's Columbus Laboratories on March 6, 1967, dealing with accelerated crack propagation in titanium has been issued by the Defense Metals Information Center.[22] Included are 15 informal papers and discussions by participants on the stress-corrosion cracking of titanium alloys by methanol, halogenated hydrocarbon, and other solutions.

The corrosion behavior of Ti-6Al-4V in commercial Freon IF with, and without 0.3 ppm chlorine gas has been studied by Aerospace Corporation.[23] Metallographic analysis and mechanical-property measurements revealed no cracking after 72 hours' exposure of welded and nonwelded tensile specimens stressed to 80 percent of the 0.2 percent offset yield strength.

The stress-corrosion-cracking behavior of some 30 commercial titanium alloys has been determined by the Naval Research Laboratory to provide guideline information and determine the underlying principles that affect stress-corrosion cracking.[24] Tests were conducted in 3.5 percent NaCl solution with precracked cantilever beam specimens. Weld specimens were included in the program. The results indicated that there was no correlation between mechanical properties and susceptibility to stress-corrosion cracking.

Fracture toughness and the stress-corrosion cracking of welded 1-inch thick titanium-alloy specimens has also been studied by the Naval Research Laboratory.[25] The stress-corrosion tests were performed in 3.5 percent NaCl solution using

precracked cantilever beam specimens. Alloys studied included Ti-6Al-4, Ti-6Al-2Mo, Ti-6Al-6V-2Sn, Ti-5Al-3V-1Mo, Ti-7Al-2Cb-1Ta, Ti-7Al-1Mo-1V, Ti-5Al-2Sn-2Mo-2V, Ti-7Al-2.5Mo, and Ti-6Al-2Cb-1Ta-0.8Mo. There did not appear to be any correlation between fracture toughness and stress-corrosion-cracking resistance of the materials.

Studies on the effect of hydrogen and microstructure on the stress-corrosion cracking of titanium alloys are continuing at Douglas.[26] Different amounts of hydrogen (27 and 100 ppm) were introduced in Ti-8Al-1Mo-1V at 1600, 1800, and 2000 F, followed by an air quench. Subsequent tests with notched specimens in ambient 3 percent NaCl solution revealed that the 1600 F solution treatment was susceptible to stress-corrosion cracking at these hydrogen concentrations, but that the 1800 and 2000 F treatments were not.

The morphology of stress-corrosion cracks in titanium alloys has been studied by Boeing.[27] Precracked specimens were exposed to 3.5 percent NaCl solution. Comparisons of electron fractographs of cracks and electron micrographs of the structures in alpha-beta Ti-8Al-1Mo-1V and Ti-6Al-4V alloys revealed a cleavage failure in the alpha phase and a ductile rupture in the beta phase. Coplanar dislocation arrangements were found in Ti-5Al-4V and Ti-8Al-1Mo-1V but not in Ti-4Al-Mo-1V, which correlated qualitatively with susceptibility of these alloys to cracking under these exposure conditions.

The stress-corrosion-cracking behavior of Ti-8Al-1Mo-1V alloy in NaCl and methanol is being studied at The Ohio State University.[28] Slow crack growth in precracked tensile-type specimens occurred over a range of -960 to 2040 mv (SHE) in saltwater, suggesting that hydrogen evolution is not a necessary factor in crack propagation. Current densities of 1.5 amp/cm² were estimated during the active propagation of a rapidly advancing crack in methanol-water-salt solution.

The influence of microstructure on the stress-corrosion fracture path in titanium alloys is being studied at Boeing.[29] Results obtained with precracked notched specimens in 3.5 percent NaCl solution indicated stress-corrosion-cracking susceptibility in the alpha phase in Ti-8Al-1Mo-1V, Ti-6Al-4V, and Ti-Al-3Mo-1V, in martensite in Ti-6Al-2.5Sn, and in the beta phase in Ti-13V-11Cr-3Al. Stress-corrosion-cracking susceptibility could not be correlated with any one or combination of microstructural features. Immunity to cracking (at least in the three immune phases of Ti-8Al-1Mo-1V alloy) appeared to be related to high molybdenum and vanadium content and low aluminum and oxygen content. Thus, the basic cracking mechanism was concluded to be surface controlled.

Boeing has also used wedge-force loading of center-cracked sheet specimens to determine whether stress-corrosion cracking depends on an applied crack-tip stress-intensity factor or on net-section stresses.[30] With this loading, crack extension causes a decreasing stress-intensity factor at the crack tip, while the net-section stresses increase. Thus, when the stress-corrosion crack growth is arrested in this specimen, the dependency on stress intensity is indicated. The stress intensity at arrest for Ti-8Al-1Mo-1V alloy agreed well with K_{scc}

values determined by other techniques that establish crack initiation thresholds through multiple tests.

Research on the stress-corrosion cracking of notched titanium in seawater is continuing at the Marine Engineering Laboratory.[31] Results to date with titanium-aluminum alloys indicate that a critical amount of coherent Ti₃Al precipitate will cause seawater stress-corrosion cracking. As the quantity of Ti₃Al was increased, the sensitivity of the alloy to cracking also increased. The reduction of aluminum and oxygen contents and the addition of isomorphous beta stabilizers suppressed the formation of Ti₃Al and improved the resistance of titanium-aluminum alloys to cracking in seawater. Minor additions of less than 0.5 percent of the eutectoid formers, nickel, iron, and manganese, increased the cracking sensitivity of Ti-7Al-2Cb-1Ta, while the addition of 0.09 percent palladium made this same alloy resistant to cracking. A minimum of 0.250 percent oxygen in unalloyed titanium induced cracking in seawater.

The effect of high-altitude supersonic airflow conditions on the hot-salt cracking of titanium has been investigated at Lockheed.[32] Wind-tunnel tests were conducted for a total of 50 hours' exposure under each 2.5 supersonic flow conditions at a pressure equivalent to 70,000-ft altitude and temperatures of 600 and 700 F. Duplex-annealed Ti-8Al-1Mo-1V and mill-annealed Ti-6Al-4V alloys were used in self-stressed specimens. The results demonstrated that these simulated supersonic-flight conditions did not eliminate hot-salt cracking. However, the cracking was not as severe as in static laboratory tests at the same temperature, presumably because of the removal of some of the salt coating by the high velocity air.

A summary report has been issued by Northrop on the hot-salt stress-corrosion cracking of Ti-6Al-4V, Ti-8Al-1Mo-1V, Ti-13V-11Cr-3Al, Ti-6Al-6V-2Sn, and Ti-679 alloys.[33] At 450 F, only mill-annealed Ti-8Al-1Mo-1V alloy exhibited cracking. Threshold values for cracking were found to be between 0.35 and 0.50 of the yield strength at 550 F and between 0.25 and 0.45 of the yield strength at 650 F. At stress levels just above threshold values, crack nucleation times were much longer with thermal cycling than during continuous exposure at temperature. Studies on the kinetics of the formation and decomposition of TiCl₂ on NaCl-coated titanium alloys indicated the possibility of eliminating the hot-salt cracking of titanium alloys above 550 F by thermal cycling in such a manner that the time at temperature is less than that required to form TiCl₂ and that the time at room temperature is greater than that required to decompose TiCl₂.

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